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THEORETICAL STUDIES ON EXCITED MOLECULAR VIBRATIONAL STATES. (U)

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Summary of Important Results by B. Ritchie* and B. R. Tambe.

*Principal Investigator.

Abstract. Calculations are performed for the scattering of electrons from H_2^+ in the "fixed-nuclei" approximation. It is assumed that amplitudes for rotationally and vibrationally inelastic scattering can be constructed knowing the parameters of the elastic scattering for the fixed nuclei ("adiabatic nuclei theory"); thus emphasis has been on the determination of accurate elastic scattering parameters in the fixed-nuclei approximation. The hydrogen molecular ion was chosen as a prototype target because its states are known exactly (in the Born-Oppenheimer theory) or can be represented accurately using variational theory. Calculations are carried out for coupled and uncoupled single-center partial waves. Significant disagreement with earlier work is obtained based on the projection technique used to obtain the static-exchange potential. In particular the p-wave phase shifts (or eigenphases in the coupled approximation) are significantly smaller when the projection onto the space of the target electron is made with the full target $1s\sigma_g$ eigenstate, rather than only its zeroth-order component.

Introduction:

In the last few years a great deal of research effort has been devoted to the scattering of electrons from atoms and molecules. The theoretical framework, developed to deal with electron-atom scattering within the limitations of present generation of computers, is being extended to handle the scattering of electrons from diatomic molecules. In many cases these efforts have been at least qualitatively successful in explaining the experimental observations.^(1, 2) The principal obstacle, in making relativistic calculations for electron molecule scattering, is the great number of exchange terms that arise due to the fact that the molecular wave function is an essentially multicenter function. For complex multicenter targets the only realistic approach is to use some approximation scheme which replaces these exchange terms with a simplified potential. The so-called pseudo-potential method has been highly successful in dealing with closed subshells.⁽¹⁾ As yet, very little is known about the scattering of electrons from molecular ions and molecules with incomplete subshells.

The lack of knowledge about scattering from molecular ions results in a serious disadvantage for computational work in photoionization of diatomic molecules. Most work in this field is based on the use of very crude continuum wave functions which are likely to be valid only in the asymptotic region.⁽³⁾ As a result, even the most careful work in photoionization has failed to explain some of the experimentally observed features of molecular

Recent advances in photoelectron spectroscopy, resulting from rapid development of laser technology, have generated great interest in theoretical work on photoionization. As a first step in our work on photoionization of complex molecules, we have studied the scattering of electrons from H_2^+ . This target is interesting for several reasons despite its experimental inaccessibility. It is the only molecular ion whose electronic wave function is known exactly. Also, some work already exists on this problem.^{4,5} This work can be used to provide several guidelines for our work. The principal drawback of the existing work is that the computational methods cannot be easily generalized to more complex targets. Thus the single center wave function used in this calculation has been explicitly calculated, instead of being generated from a known multicenter wave function. Besides being impractical for complex targets, the advantage of starting from an exact wave function and then being able to generate any number of single center components to test convergence properties is lost.

In Ref. (4) it has been shown that the induced polarization of H_2^+ target plays an important role in the scattering mechanism. In that work, these effects have been accounted for through the use of the polarized orbital method. This method has been previously shown to yield very dependable results in electron atom scattering.⁽⁶⁾ However, for molecules with several electrons, this method would be quite unsuitable

because of the several new exchange terms that it generates. We have, therefore, used a simple parameterized polarization potential which produces the correct long range behavior. Such a potential has been widely used in most work on electron molecule scattering.⁽²⁾ Moreover, it appears to be consistent with the level of approximation employed for the calculation as a whole. We find that such a potential produces surprisingly good agreement with the more elaborate polarized orbital method.

It is natural to expect that it is possible to approach the photoionization of complex targets by a suitable combination of pseudo-potential method and direct handling of some exchange terms. With the addition of a one parameter polarization potential one can include all the major interactions involved in this problem. This can lead to at least a qualitative understanding of the photoionization of diatomic molecules. It is therefore essential to develop computational techniques for the simplest of these problems before more complicated targets can be approached with confidence.

Theory:

The method of close coupling approximation has been highly successful in low energy electron atom scattering. It has been recently extended to low energy electron molecule scattering. In this method the wave function corresponding to the electron and molecule is written as an expansion in terms of a basis set corresponding to the states of the molecule. The expansion coefficients are then the continuum wave function corresponding to different channels. The difficulty with regard to molecules arises from the extra degrees of freedom, namely rotational and vibrational motion of the molecule. These give rise to a number of closely spaced energy levels for the molecule. Any rigorous expansion must include all of these levels for low energy scattering. However, the splitting between different rotational and vibrational levels is quite small. This also means that the time scale on which rotational or vibrational motion takes place is quite large compared to the time scale involved in electronic motion. As a result, it is possible to assume that the nuclei do not move during the collision. This is known as the fixed nuclei approximation. The R-matrix obtained in this approximation can be used to obtain the transition matrix for transitions between different rotational vibrational levels. In⁽⁴⁾ it has been shown that the orientation of the molecular axis enters the problem only in a geometrical way, apart from a m dependence of the solution. The validity of these approximations has been checked recently.⁽⁷⁾ These approximations make our task quite simple,

namely, to calculate phase shifts in fixed nuclei approximation from which all the physical properties of interest can be deduced through algebraic manipulations. The fixed nuclei approximation breaks down in two cases: (a) if the incident energy is too low and (b) in case of a resonance. In our present work we shall be concerned with neither of these situations.

The formulation of the $e^-H_2^+$ scattering closely follows along the lines of Burke and Sinfailam.⁽⁸⁾ Hence we will only indicate the important steps.

We start by writing the wave function as

$$\psi = \phi(r_1)F_p(r_2) \pm \phi_\alpha(r_2)F_p(r_1) \quad (1)$$

where ϕ is the wave function for the H_2^+ ion and F_p is the wave function of the projectile. The \pm sign refers to singlet and triplet scattering.

The Hamiltonian for such a system is

$$H = \frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{1}{r_{A1}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}} - \frac{1}{r_{B2}} + \frac{1}{r_{12}} + \frac{1}{r_{AB}} - E$$

where ∇_1^2 and ∇_2^2 are kinetic energy operators for electrons 1 and 2, and A and B are the positions of the two nuclei. r_{A1} refers to the distance between the nucleus at A and the electron at 1. Other symbols have similar meaning.

The wave function $\phi_\alpha(r)$ for the hydrogen molecular ion is of the form

$$e^{-\alpha r_a} + e^{-\alpha r_b}$$

This can be transformed into a single center wave function by using the method of Harris and Michels.⁽⁹⁾ We then get

$$\phi_{\alpha}(r) = \sum_s \frac{1}{r} U_s^{\alpha}(r) Y_s^{\lambda_{\alpha}}(\hat{r}) \quad (2)$$

where α refers to the m value and \hat{r} to the angular coordinate.

The projectile wave function is expanded as

$$F_p(r) = \sum_s \frac{1}{r} f_s^p(r) Y_s^{\lambda_p}(r) \quad (3)$$

We set up close-coupling equations by using Kohn variational principle. This starts out with the integral

$$I = \langle \Psi, (H-E)\Psi \rangle$$

The direct term contains a potential

$$\langle \phi_{\alpha}(r_1), \left(\frac{1}{r_{12}} - \frac{1}{r_{A2}} - \frac{1}{r_{B2}} \right), \phi_{\alpha}(r_1) \rangle \quad (4)$$

Substituting (2) in (4) and using the standard spherical harmonic expansion for $\frac{1}{r_{ab}}$ terms this potential reduces to the form

$$V(r) = \sum_{\lambda} V_{\lambda}(r) P_{\lambda}(\cos \theta) \quad (5)$$

We have written a computer program to calculate $U_s^{\alpha}(r)$ in eqn. (2) and $V_{\lambda}(r)$ in eqn. (5). These programs were checked quite thoroughly. We were able to reproduce the potential for N_2 given by Faisal⁽¹⁰⁾ as a check on our program.

The remaining part in the direct term is the Hamiltonian for H_2^+ and the kinetic energy operator for the projectile. Hence finally the direct term is

$$\langle F_p(r), \left\{ -\frac{1}{2} \nabla^2 + V(r) - (E - E_{H_2^+}) \right\} F_p(r) \rangle \quad (6)$$

Substituting eqn. (3) in eqn. (6) we get the expression (13) of ref. 8. The only difference is that our direct potential contains a net monopole moment.

The exchange term has the form

$$\left\langle F_p(r_1)\phi_\alpha(r_2) \left| -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_{A1}} - \frac{1}{r_{B1}} - \frac{1}{r_{A2}} - \frac{1}{r_{B2}} + \frac{1}{r_{AB}} + \frac{1}{r_{12}} - E \right| F_p(r_2)\phi_\alpha(r_1) \right\rangle \quad (7)$$

$$\left\langle F_p(r_1)\phi_\alpha(r_2) \left| -\frac{1}{2}\nabla_2^2 - \frac{1}{r_{A2}} - \frac{1}{r_{B2}} + \frac{1}{r_{12}} - \frac{1}{2}k^2 \right| F_p(r_2)\phi_\alpha(r_1) \right\rangle \quad (8)$$

Using the Hermitian property we can replace the first three terms by the electronic energy of H_2^+ .

$$\left\langle F_p(r_1)\phi_\alpha(r_2) \left| F_p(r_2)\phi_\alpha(r_1) \right\rangle (E_{H_2^+}^e - \frac{1}{2}k^2) \right\rangle$$

$$\left\langle + F_p(r_1)\phi_\alpha(r_2) \left| \frac{1}{r_{12}} \right| F_p(r_2)\phi_\alpha(r_1) \right\rangle \quad (9)$$

The second term here is the standard exchange term and it can be treated in the usual fashion. First term gives a non-zero contribution only if the projectile wave function is not orthogonal to the molecular orbital. For orbitals with g symmetry the expansion (2) contains only even terms and hence the first term will be non-zero only for partial waves with even angular momentum.

Next we use eqn. (2) and eqn. (3) in eqn. (9) and obtain a set of coupled integro-differential equations. Since m, the magnetic quantum number and the parity are conserved there is no coupling between different values of these quantum numbers.

The coupled set of equations can be solved by the non-iterative integral equation method outlined by Smith and Henry.⁽¹¹⁾ By applying

appropriate boundary conditions for Coulomb scattering we can then obtain R matrix or the phase-shifts. These procedures are quite standard and need not be described in detail here.

As we have remarked earlier, we have included the effect of polarization by adding to (5) an induced polarization potential of the form (ref. 2).

$$V_{pol} = - \left(\frac{\alpha_0(R)}{r^4} + \frac{\alpha_2(R)}{r^4} P_2(\cos\theta) \right) (1 - e^{-(r/r_0)^6}) \quad (10)$$

Where α_0 and α_2 are the isotropic and anisotropic part of dipole polarizability. These values have been calculated by A. Rahman. (12)

Results and Discussion:

The method employed by us to calculate single center components of the hydrogen molecular ion wave function is different from that used in Ref. 4 where only the first two components have been calculated. In Table 1 we compare our first two components (corresponding to $\ell = 0$ and 2) with those of Ref. 4. The difference, especially for the $\ell = 2$ component, is quite large. This will affect both the direct and the exchange potentials. However, for direct potential, the dominant term is electric monopole. In Ref. 4, this has been normalized to unity through the use of a multiplying factor. In our approach this term comes out very close to unity if we retain sufficient number of single center components. In view of the long range behaviour of the monopole potential we did normalize this term exactly to one so that the proper boundary conditions may be applicable exactly. Higher order potentials from Ref. 4 are not available, hence we cannot comment on the differences between those.

We have retained up to $S = 14$ components in eqn. 2 in evaluating the direct potential.

For molecular scattering problems the main computational difficulty arises from the exchange potential. The need for making spherical harmonic expansion for both $1/r_{12}$ term and the molecular wave function gives rise to a very large number of exchange terms. The problem is further complicated due to coupling of different partial waves since the total angular momentum is not a conserved quantum number. We must retain sufficient terms in eqn. (3) to get convergence. In the resulting coupled equations each single center component retained in eqn. (2) gives rise to several exchange terms. Hence in making the calculation it is important to study the convergence of phase shifts as a function of the number of terms retained in eqn. (2). Then, in a full calculation we can retain the minimum number of exchange terms that is sufficient for obtaining convergence. A look at expression⁽⁹⁾ shows that the part of exchange term arising from the overlap of projectile wave function with the molecular ion wave function complicates the study of exchange terms. This can be avoided by studying p wave scattering which makes this overlap term zero. Tables 2 and 3 show the result of such a study. In Table 2 we show phase shifts for triplet p wave scattering. This partial wave is chosen because of the good agreement between our results and those of Ref. 4. The phase shifts here are relatively unchanged as more and more exchange terms are added. Thus a Zeroth order calculation gives almost converged results for this case, while approximation b gives converged results. However, this

observation is not generally valid as demonstrated in Table 3 for singlet p wave with $m = 0$. It is obvious that all exchange terms arising from $\ell = 2$ single center components should be retained to obtain converged results in all cases. Terms arising from $\ell = 4$ do not make a large difference in either case. Table 3 also shows large differences between our results and those of Ref. 4. For higher energy the role of exchange terms becomes less important and the differences become smaller. These observations are valid for all the other cases that we studied. The singlet terms are important for photoionization work and one of our objectives is to obtain converged results for singlet p waves. We will, therefore retain all the terms arising from $\ell = 0, 2$ components in eqn. (2) in the work that follows.

It has been noted before that the field produced by a molecule is necessarily non-central. As a result different partial waves get coupled to each other. Therefore, in eqn. (3) we must include an adequate number of partial waves to produce convergence. It is known that in the united atom limit ($e^- - \text{He}^+$ scattering) even d waves make negligible contribution. It is obvious that in $e^- - \text{H}_2^+$ case higher partial waves will be important since the charge distribution of a molecule occupies a greater region of space. In our next calculations we have studied convergence of phase shifts as the number of partial waves retained in eqn. (3) is increased. In the coupled case all the results are difficult to present in one single table in a meaningful way. We have, therefore, presented the dominant eigenphase in Table 4 and 5. Table 4 shows the s wave eigenphase for $^1\Sigma_g$ scattering. It is seen that the addition of d waves gives quite accurate results. The next partial wave makes quite a small change.

In the case of odd parity the situation was even simpler. It was found that the addition of f waves made an extremely small difference except in the case of $^1\Sigma_u$ scattering. In our work we found the $^1\Sigma_u$ phase shifts to be quite sensitive to all changes in the scattering potential. One of our aims in this study was to obtain reliable continuum wave functions for photoionization of H_2 . In view of the importance of $^1\Sigma_u$ case for photoionization we studied this in some detail. It is found that retention of p and f waves gives converged results. For all other odd parity cases even f wave made negligible contribution. It is thus obvious that retaining terms upto $l = 3$ in eqn. (3) gives converged phase shifts.

We find that the agreement between our results and those of Ref. 4 is quite good for triplet states. For singlet scattering the agreement is quite poor at low energy but improves significantly as the incident energy is increased. These facts can be quite easily explained on the basis of our better treatment of the exchange terms.

In all of our work so far we have neglected the effect of polarization. Several elegant methods have been developed for electron atom scattering for this purpose. In Ref. 4 one of these methods, namely polarized orbital method has been applied to $e^-H_2^+$ scattering. For obvious reasons this cannot be extended to more complicated systems. Hence, it is common to use a potential of the form (10) to include induced polarization effect. The existence of the rather elaborately obtained results in Ref. 4 encourages us to study the applicability of (10). Since our results for triplet scattering agree quite well for some cases,

we could use them for the selection of the parameter r_0 . This parameter is essentially used for cutting off the polarization potential at close range. It is quite apparent that this short range should be approximately equal to the interatomic distance in order to avoid any spurious short range correlation. We initially set this parameter equal to the interatomic distance. Then this parameter is varied to check the sensitivity of the phase shifts to variations of this parameter. We show our results in Table 6. From this it is obvious that a small error in choice of r_0 will still keep the overall results consistent with the level of approximations that can be generally attained in electron-molecule scattering calculations at present. It was shown in Table 2 that for the $^3\Sigma_u$ scattering our results agree well with those of Ref. 4. Hence we perform a calculation for this partial wave with the inclusion of polarization potential. The cut-off parameter was chosen to be 2.0. Table 7 shows our results. These are compared with the polarized orbital results of Ref. 4. It is apparent that this choice of r_0 is quite appropriate.

From the preceding arguments we can now proceed to obtain converged phase shifts for $e^-H_2^+$ scattering in the fixed nuclei approximation. We construct a direct potential of the form of eqn. 5 containing up to 15 terms. Of these only a limited number (depending upon the highest partial wave) contribute to the direct potential in any case. We cut off eqn. 2 at $s = 2$ for retaining exchange terms and eqn. 3 at $s = 3$ partial wave. A polarization potential of the form given by eqn. 10 is employed with $r_0 = 2.0$. We have obtained results for all the cases of interest. These have been tabulated in Table 8. It is convenient to give these in

terms of two eigenphases and a mixing parameter.⁽¹³⁾ We have also obtained phase-shifts without a polarization potential. These have not been presented here to avoid repetition. However, these may be obtained by writing to one of the authors.

We have thus obtained converged phase shifts from which rotational excitation cross-sections can be obtained in a straightforward manner.⁽¹⁴⁾ It is also possible to obtain good photoionization cross-sections by obtaining a continuum wave function which takes into account all the major potentials.

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Table 1

r	Ref. 4		This Work	
	U_0	U_2	U_0	U_2
0.2	0.220	0.00257	0.186	0.00309
0.6	0.597	0.0569	0.528	0.0717
1.0	0.794	0.157	0.747	0.213
1.4	0.7625	0.163	0.744	0.230
1.8	0.6215	0.127	0.628	0.187
2.2	0.464	0.0898	0.488	0.140
2.6	0.329	0.0604	0.361	0.0995
3.0	0.224	0.0393	0.259	0.0691
3.4	0.1485	0.0251	0.181	0.0471
4.0	0.0773	0.0125	0.1023	0.0258
5.0	0.0242	0.00369	0.0374	0.00909
7.5	0.00107	0.000149	0.002534	0.000582

Single center components for the hydrogen molecular ion wave function. Subscript denotes the value of ℓ .

Table 2

 ${}^3\Sigma_u$

Approximation Energy (Ryd.)	a	b	c	Ref. 4
0.1	1.112	1.185	1.187	1.150
0.3	1.015	1.077	1.079	1.048
0.5	0.938	0.993	0.994	0.970

p wave triplet phase shifts for $m = 0$ (${}^3\Sigma_u$)

a terms of the order $[u_2(r)]^2$ and higher are excluded as in ref. 4, where $u_2(r)$ is the single center component corresponding to $\ell = 2$ in eqn. (2).

b All terms of the order $[u_2(r)]^2$ are retained.

c Terms up to order $[u_4(r)]^2$ are retained.

Table 3

 $1\Sigma_u$

Approximation → Energy (Ryd.)	d	Ref. 4 Zeroth order result	a	Ref. 4 first order result	b	c
0.1	0.366	0.450	0.2572	0.325	0.114	0.111
0.3	0.395	0.462	0.302	0.345	0.174	0.171
0.5	0.415	0.470	0.336	0.363	0.225	0.223

a, b, c - as in Table 2.

Ref. 4 first order result is similar calculation to a

d - calculation similar to Zeroth order of Ref. 4 where exchange terms involving $u_2(r)$ are dropped.

Table 4

 $1\Sigma_g$

$\eta_{00} \rightarrow$ Energy (Ryd.) \downarrow	s	s + d	s + d + g
0.1	-0.2938	-0.2639	-0.2588
0.5	-0.3670	-0.3462	-0.3407
0.9	-0.4151	-0.3993	-0.3937
2.0	-0.4794	-0.4644	-0.4595

Variation of s wave eigenphase as more and more terms are retained in eqn. (3)

Table 5a

 $^1\Sigma_u$

$\eta_{11} \rightarrow$ Energy (Ryd.)	p	p + f	p + f + h
0.1	0.111	0.207	0.229
0.5	0.223	0.334	0.361
0.9	0.289	0.405	0.431
2.0	0.335	0.444	0.468

Variation of p wave eigenphase with the addition of partial waves.

Table 5b

 $1\pi_u$

Energy	η_{11}	η_{11}
	p	p + f
0.1	-0.343	-0.339
0.5	-0.314	-0.309
0.9	-0.287	-0.282
2.0	-0.240	-0.234

Table 6

 1_{Σ_g}

$r_0 \rightarrow$ Energy \downarrow	∞ (no polarization)	1.75	2.0	2.25
0.1	-0.264	-0.182	-0.191	-0.197
0.5	-0.346	-0.257	-0.268	-0.276
0.9	-0.399	-0.304	-0.317	-0.329

Variation of η_{00} with the variation of the cut-off parameter (r_0) in the polarization potential.

Table 7

 $^3\Sigma_u$

Energy	This Work	Ref. 4
0.1	1.307	1.308
0.5	1.093	1.105
0.9	0.956	0.974

P - wave phase-shifts in an uncoupled calculation with polarization potential. ($r_0 = 2.0$)

TABLE 8a

 Σ_g

Singlet				Triplet		
Energy (Ryd.) ϵ		η_{00}	η_{22}	ϵ	η_{00}	η_{22}
0.10	-0.1877	-0.192	0.166	0.1769	0.100	0.301
0.3	-0.2214	-0.234	0.192	0.0813	0.0562	0.358
0.5	-0.2358	-0.268	0.216	0.0378	0.0168	0.399
0.7	-0.2396	-0.295	0.236	0.0146	0.0184	0.429
0.9	-0.2376	-0.317	0.254	0.00144	-0.0497	0.451
2.0	-0.1887	-0.386	0.325	0.01017	-0.173	0.500
4.0	-0.0790	-0.422	0.392	0.0306	-0.285	0.512

TABLE 8b

Energy (Ryd.)	Σ_u					
	Singlet			Triplet		
	ϵ	η_{11}	η_{33}	ϵ	η_{11}	η_{33}
0.10	-0.00179	0.490	0.050	-0.0033	1.423	0.054
0.30	0.0128	0.512	0.064	0.0008	1.299	0.075
0.50	0.02739	0.529	0.075	0.008	1.205	0.093
0.70	0.04167	0.540	0.0848	0.0150	1.1287	0.111
0.90	0.0556	0.545	0.0937	0.0232	1.065	0.127
2.00	0.1309	0.528	0.131	0.0736	0.829	0.190
4.00	0.2880	0.438	0.164	0.194	0.590	0.237

Energy (Ryd.)	π_u					
	Singlet			Triplet		
	ϵ	η_{11}	η_{33}	ϵ	η_{11}	η_{33}
0.10	-0.0096	-0.189	0.0417	0.0356	0.301	0.045
0.30	-0.266	-0.185	0.0537	0.0931	0.256	0.062
0.50	-0.0373	-0.183	0.0636	0.173	0.220	0.076
0.70	-0.045	-0.180	0.0723	0.295	0.192	0.086
0.90	-0.0509	-0.178	0.0802	0.481	0.172	0.092
2.0	-0.065	-0.169	0.112	-0.304	0.041	0.176
4.0	-0.0619	-0.161	0.137	-0.133	-0.0379	0.20

TABLE 8C

d wave phase shifts (π_g and δ_g)

Energy (Ryd.)	π_g		δ_g	
	Singlet	Triplet	Singlet	Triplet
0.1	0.097	0.195	-0.029	0.014
0.3	0.104	0.233	-0.029	0.029
0.5	0.110	0.256	-0.031	0.038
0.7	0.114	0.271	-0.032	0.042
0.9	0.117	0.279	-0.034	0.045
2.0	0.120	0.271	-0.046	0.033
4.0	0.107	0.220	-0.066	0.005